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芸香科九里香属及美栌木属的化学分类

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摘要 通过化学分析证明,美栌木与九里香属内的九里香组植物较为接近,两者均含月橘烯碱及8-戊烯化香豆精,而棕茎组植物则与黄皮属植物亲缘关系较近。据此肯定了 Tanaka 的观点,认为棕茎组比九里香组原始。黄皮族内的亲缘关系亦可作如下推断: 小芸木属→山小桔属→黄皮属→九里香属棕茎组→九里香属九里香组→美栌木属。

关键词 化学分类;月橘烯碱;8-戊烯化香豆精;黄皮族;九里香属; 九里香组;棕茎组;美栌木属

前 言

Swingle[14-15] 将芸香科 Rutaceae 中的柑桔亚科 Aurantioideae 分为两个族,并将其中的黄皮族 Clauseneae 再分为三个亚族;这三个亚族顺序为小芸木亚族 Micromelinae、黄皮亚族 Clauseninae 和美栌木亚族 Merrilliinae。小芸木亚族和美栌木亚族各自只有一个属,而黄皮亚族则包含三个属。从形态上判断,黄皮族是个自然的分类群,其内的五个属有着线性的亲缘关系(Linear relationship),由最原始的小芸木属 *Micromelum* 顺序进展为山小桔属 *Glycosmis*、黄皮属 *Clausena*、九里香属 *Murraya* 和美栌木属 *Merrillia*。植物化学分析基本上亦支持这种线性的亲缘关系,特别是3-甲基咔巴唑生物碱的氧化程度和复杂性,由山小桔属的 CH_3 和 C_{13} 的类型,进展为黄皮属的 CHO 和 C_{18},及九里香属的 COOH 和 C_{23}; 黄酮的分布则显示由黄皮亚族进展到美栌木亚族[18-19]。

对九里香属的化学成分及分类处理等,一些学者做了不少工作[1,5,7-13,16]。根据化学与形态上的差异,我们在前报[1]中同意 Tanaka[16] 的处理,将九里香属分为两个组,即九里香组 Murraya Sect. Murraya 和棕茎组 Murraya Sect. Bergera。

但有些问题尚未弄清楚,特别是九里香属内的两组植物有何亲缘关系?Tanaka[16]将棕茎组置于九里香组之前,认为前者接近小芸木属,而后者则接近美栌木属。但Swingle[14,15]则将属于九里香组的植物列于棕茎组植物之前,显示前者较后者为原始; 黄成就[2,3] 也同意这种观点。这两种相反的观点对推测及解释两个组的咔巴唑生物碱和戊烯化吲哚类化合物的生源有直接的关系,而且对判断属内的特征演化,评定特征之间的相对进化程度有决定性的影响; 在进一步了解属内各种的亲缘关系时 [例如编订分歧指数 Index of divergence 和绘制华纳分歧图 Wagner divergence diagram],这些判断亦会有很大的影响。但在缺少客观数据支持的情况下,我们发现难以在两个观点中作出取舍。

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1) 2) 3) 4) 5) 6) 见英文摘要的脚注。

为了解决九里香属内两个组之间的亲缘关系问题，我们决定要对九里香属外的品种进行分析，希望从而找到提示。其中最有兴趣的是美栌木 *Merrillia caloxylon* (Ridley) Swingle，目前文献报道只见有泽兰因 (Eupatorin) 和少量黄酮类成分[4,6]。

虽然美栌木属隶属于美栌木亚族，与包含九里香属的黄皮亚族不同，但 Tanaka[16,17] 认定美栌木与九里香组接近，而 Swingle[14,15] 在讨论美栌木时亦提到它可能由千里香 *Murraya paniculata* (L.) Jack 种群的干系演化出来。假如他们的推断正确的话，我们估计美栌木可能亦拥有抗着床成分月橘烯碱及 8-戊烯化香豆精，这对开发月橘烯碱的天然来源亦有帮助。

材料与方法

材料：美栌木根皮和茎皮采自新加坡植物园，凭据标本(Mohd. Ali Rahim *s. n.*)存于香港中文大学生物系标本室及中国科学院华南植物研究所。另一份根皮采自马来西亚森林研究所的树木园，凭据标本 (FRI 28795) 存于该所的标本室内。

月橘烯碱、香豆精和咔巴唑类的提取、分离和鉴定，按前报[1]的方法一样，而泽兰因的鉴定用 UV、IR、^{1}H NMR 和 EIMS。

结果和讨论

分析的结果显示美栌木的根皮和茎皮含有月橘烯碱 Yuehchukene (I)、西伯里素 (Sibiricin) (II)、番巴洛辛 (Phebalosin) (III)、3-(3-甲基-1，3-丁二烯)吲哚 (IV) 和泽兰因 (V) (图1)。详细的化学数据另文发表1)。

通过美栌木的化学分析，证明美栌木的确与九里香属的九里香组植物有密切的关系，两类植物均含月橘烯碱和 8-戊烯化香豆精，但未见含有咔巴唑类成分，而且美栌木的根皮和茎皮跟九里香组的植物一样同为稻秆黄带白色，种子外皮有纤毛，又与翼叶九里香 *Muraya alata* Drake 一样于叶梗上有叶翼。但美栌木的花长喇叭型，长 55—60 mm.，比芸香科中其他的花大，浆果椭圆形，长达 10 cm、宽达 8 cm，外皮厚实，瘤状起伏不平，剖开时流出极粘之乳汁，内藏种子多粒(达 30 粒以上)。美栌木分布于马来半岛和苏门答腊北部[15]，据马来亚大学植物系 David Jones 教授云，该树在新马一带已不见于野外，目前只限于园林种植，这点对开发美栌木作为月橘烯碱的新来源有一定的局限性。

在证实美栌木与九里香组的植物含相同类型的成分外，我们尚可推断棕茎组的植物与黄皮属及山小桔属较为接近，因为它们都含咔巴唑生物碱，而未见有月橘烯碱和 8-戊烯化香豆精。根据化学成分，我们接受 Tanaka[16-17] 的结论，相信九里香属内棕茎组的植物较九里香组的为原始，前者与黄皮属接近，而后者(特别是翼叶九里香)与美栌木属相近。我们估计黄皮族内的亲缘关系可以归纳如下：

小芸木属→山小桔属→黄皮属→九里香属棕茎组→九里香属九里香组→美栌木属

根据九里香属两组的化学分类关系，我们相信可以进一步判断下列特征较为原始：根皮及茎皮污棕色，果球形及紫黑色，含种子少数，种皮无纤毛，花小，叶梗无叶翼。相对

1) Kong, Y. C. et al., 1987: The Biochemical Systematics of Merrillia in relation to Murraya, the Clauseneae, and the Aurantioideae, *Biochemical Systematics and Ecology* (submitted).

图 1　美栌木的化学成分

Figure 1　Chemical constitutents of *Merrillia caloxylon*

(I) Yuehchukene 月橘烯碱，(II) Sibiricin 西伯里素，(III) Phebalosin 番巴洛辛，(IV) 3-(3-methyl-buta-1, 3-diene) indole，3-(3-甲基-1，3-丁二烯) 吲哚。(V) Eupatorin 泽兰因

地，根皮及茎皮稻秆黄白色，果椭圆形及红色或黄绿色，含种子多数，种皮有纤毛，花大，叶梗具叶翼等特征均较为先进(表 1)。凭此我们或可进一步分析九里香属内甚至黄皮亚族内的种间亲缘关系。

表 1　九里香属与美栌木属特征的演化关系

Table 1　Relative advancement of the character states in *Murraya* and *Merrillia*

Character 特　征	Murraya sect. Bergera 棕茎组	Murraya sect. Murraya 九里香组	Merrillia 美栌木属
Root bark 根　皮	dark brown 污棕色	straw-colored or pale whitish 稻秆黄白色	straw-colored or pale whitish 稻秆黄白色
Stem bark 茎　皮	dark brown 污棕色	straw-colored or pale whitish 稻秆黄白色	straw-colored or pale whitish 稻秆黄白色
Leaf rachis 叶　梗	wingless 无叶翼	wingless or winged 无或有叶翼	winged 有叶翼
Flower 花	small 细小	bigger 较　大	much bigger 更　大
Fruit 果	purple-black 紫黑色	red 红　色	yellow-green 黄绿色
Seed 种　子	few 少　数	few 少　数	many 多　数
Seed coat 种　皮	glabrous 无纤毛	villous 有纤毛	villous 有纤毛
Yuehchukene 月橘烯碱	Absent 无	Present 有	Present 有
8-Prenylated coumarin 8-戊烯化香豆精	Absent 无	Present 有	Present 有
Carbzole 咔巴唑生物碱	Present 有	Absent 无	Absent 无

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CHEMOTAXONOMIC RELATIONSHIP BETWEEN *MURRAYA* AND *MERRILLIA* (RUTACEAE)

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Abstract Swingle[14-15] divided Aurantioideae into two tribes, one of which, Clausereae, was further divided into three subtribes, namely, Micromelinae, Clauseninae and Merrilliinae. Mic-

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romelinae and Merrilliinae each have one genus, whereas Clauseninae has three genera. Morphologically, the Clauseneae is a natural tribe; the five genera are related in a linear sequence, starting with *Micromelum* as the most primitive and progressing in sequence to *Glycosmis, Clausena, Murraya* and *Merrillia*. Chemical studies also support this linear relationship, as revealed by the degree of oxygenation and complexity of the 3-methyl carbazole alkaloids, from CH_3 and C_{13} in *Glycosmis* to CHO and C_{18} in *Clausena* and COOH and C_{23} in *Murraya*[20-21]. Distribution of flavonoids also indicates the progression from Clauseninae to Merrilliinae[18-19].

Extensive work has been conducted on the chemistry and taxonomy of the genus *Murraya* [1,5,7-13,16], and the data from these studies clearly indicate the presence of two distinct groups. Based on a combination of morphological and chemical differences, we agreed with Tanaka[16-17] in dividing *Murraya* into two sections, i.e. section Murraya and section Bergera[1].

However, our previous study[1] has not touched on the relationship between the two sections. Tanaka[16-17] placed section Bergera before section Murraya, and indicated that the former is close to *Micromelum* and the latter to *Merrillia*. Swingle[14-15], on the other hand, put taxa of section Murraya ahead of those of section Bergera, presumably suggesting that plants of section Murraya are more primitive than those of section Bergera; this arrangement was followed by Huang[2-3]. The two conflicting viewpoints would have direct bearings on the interpretation of the trends of biogenesis of prenylated indole and carbazole alkaloids, as well as on the weighing of the relative advancement of the morphological characters within the genus, such as in the assignment of indices of divergence and in the construction of Wagner Divergence Diagrams. Without more objective criteria, we find it difficult to select one of the two systems.

In order to determine the relationship between the two sections of *Murraya*, we decided to study plants of related genera, with the hope that the chemical data may shed light on the problem. A plant that attracted our attention is *Merrillia caloxylon* (Ridley) Swingle. So far, only eupatorin and a few other flavonoids have been reported from the fruit of this species[4,6].

Although *Me. caloxylon* belongs to Merrilliinae, a subtribe next to Clauseninae, Tanaka[16-17] believes that it is close to *Murraya* section Murraya. Swingle[15], also suggested that this species might have developed from the same stock that gave rise to *Mu. paniculata*. If their interpretations were accurate, we would expect that *Me. caloxylon* would also contain yuehchukene and 8-prenylated coumarins. The presence of the antiimplantation agent would not only open up a new source of the compound but also help us judge the relationship between the two sections of *Murraya*. It is in this context that we studied the chemical composition of *Me. caloxylon*.

Indeed, root and stem bark of *Me. caloxylon* were found to contain the antiimplantation indole alkaloid yuehchukene (I), and the 8-prenylated coumarins sibiricin (II) and phebalosin (III), as well as 3-(3-methyl-buta-1,3-diene) indole (IV) and eupatorin (V.) Details on the chemical profiles are reported in another paper.

Through this exercise, we have confirmed the close relationship between Merrilliinae and *Murraya* section Murraya; plants of both taxa contain yuehchukene and 8-prenylated coumarins, but no carbazole alkaloid. Root and stem bark of *Me. caloxylon,* like those of plants of section Murraya, are strawcolored to pale whitish. Its leaves also bear wings along the rachis an in *Mu. alata,* and the seeds are also villous. However, *Me. caloxylon* has long trumpetshaped flowers 55—60 mm long, much larger than those found in other rutaceous plants. Its fruit is ob-

long, up to 11 cm long and 8 cm across, bearing a thick and warty pericarp, exuding a very stick mucilage when cut, and containing numerous seeds (>30). The plant was known to exist in the Malay Peninsula and north Sumatra[15], but, according to David Jones (per. comm.) of the University of Malaya, is now only available in cultivation in Malaysia and Singapore, a limitation to any further exploitation as an additional source of yuehchukene.

Besides confirming the close relationship between *Merrillia* and section Murraya, we may also conclude that section Bergera is close to *Glycosmis* and *Clausena*, since they are known to contain carbazole alkaloids but no yuehchukene. Accordingly, we find Tanaka's arrangement more acceptable: plants of section Bergera are more primitive than those of section Murraya; the former is close to *Clausena* whereas the latter (notably *Mu. alata*) to *Merrillia*. The relationship among the gonera with in Clauseneae may be illustrated as follow: *Micromelum*→*Glycosmis*→*Clausena*→*Murraya* sect. Bergera→*Murraya* sect. Murraya→*Marrillia*.

Accordingly, we may decide that the following character states are more primitive among plants of *Murraya* and *Merrillia*: root and stem bark dark brown, leaf rachis wingless, flower small, fruit purple-black with few seeds, and seed coat glabrous. In contrast, straw-colored or pale whitish bark, winged leaf rachis, large flower, red or yellow fruit with many seeds and villous seed coat can be regarded as more advanced characters.

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Key words Chemotaxonomy; yuehchukene; 8-prenylated coumarin; Clauseneae; *Murraya*; *Murraya* section Bergera; *Murraya* section Murraya; *Merrillia*